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(54) Title: LIQUID CRYSTAL DETERGENT COMPOSITIONS (57) Abstract This invention relates to a liquid crystal composition comprising a water insoluble organic compound, a sulfonate surfactant, an abrasive, an ethoxylated alkyl ether sulfate surfactant, a cosurfactant and water.		

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LIQUID CRYSTAL DETERGENT COMPOSITIONS

Field of the Invention

This invention relates to a liquid crystal detergent composition containing an
5 abrasive. More specifically, it is of a liquid detergent composition in liquid crystal state
which when brought into contact with oily soil is superior to other liquid detergent
compositions in detergency and in other physical properties.

Background of the Invention

Liquid aqueous synthetic organic detergent compositions have long been
10 employed for human hair shampoos and as dishwashing detergents for hand washing
of dishes (as distinguished from automatic dishwashing machine washing of dishes).
Liquid detergent compositions have also been employed as hard surface cleaners, as in
pine oil liquids, for cleaning floors and walls. More recently they have proven
successful as laundry detergents too. apparently because they are convenient to use.
15 are instantly soluble in wash water, and may be employed in "pre-spotting" applications
to facilitate removals of soils and stains from laundry upon subsequent washing. Liquid
detergent compositions have comprised anionic, cationic and nonionic surface active
agents, builders and adjuvants, including, as adjuvants, lipophilic materials which can
act as solvents for lipophilic soils and stains. The various liquid aqueous synthetic
20 organic detergent compositions mentioned serve to emulsify lipophilic materials,
including oily soils, in aqueous media, such as wash water, by forming micellar
dispersions and emulsions.

Although emulsification is a mechanism of soil removal, it has been only
comparatively recently that it was discovered how to make microemulsions which are
25 much more effective than ordinary emulsions in removing lipophilic materials from
substrates. Such microemulsions are described in British Patent Specification No.
2,190,681 and in U.S. Patents 5,075,026; 5,076,954 and 5,082,584 and 5,108,643,
most of which relate to acidic microemulsions useful for cleaning hard surfaced items,
such as bathtubs and sinks which microemulsions are especially effective in removing

soap scum and lime scale from them. However, as in Serial No. 4,919,839 the microemulsions may be essentially neutral and such are also taught to be effective for microemulsifying lipophilic soils from substrates. In U.S. Patent application Serial No. 7/313,664 there is described a light duty microemulsion liquid detergent composition

5 which is useful for washing dishes and removing greasy deposits from them in both neat and diluted forms. Such compositions include complexes of anionic and cationic detergents as surface active components of the microemulsions.

The various microemulsions referred to include a lipophile, which may be a hydrocarbon, a surfactant, which may be an anionic and/or a nonionic detergent(s), a

10 co-surfactant, which may be a poly-lower alkylene glycol lower alkyl ether, e.g., tripropylene glycol monomethyl ether, and water.

Although the manufacture and use of detergent compositions in microemulsion form significantly improved cleaning power and greasy soil removal, compared to the usual emulsions, the present invention improves them still further and also increases

15 the capacity of the detergent compositions to adhere to surfaces to which they have been applied. Thus, they drop or run substantially less than cleaning compositions of "similar" cleaning power which are in microemulsion or normal liquid detergent form. Also, because they form microemulsions with lipophilic soil or stain material spontaneously, with essentially no requirement for addition of any energy, either

20 thermal or mechanical, they are more effective cleaners at room temperature and at higher and lower temperatures that are normally employed in cleaning operations than are ordinary liquid detergents, and are also more effective than detergent compositions in microemulsion form.

The present liquid crystal detergent compositions may be either clear or

25 somewhat cloudy or milky (opalescent) in appearance but both forms thereof are stable on storage and components thereof do not settle out or become ineffective, even on storage at somewhat elevated temperatures for periods as long as six months and up to a year. The presence of the cosurfactant in the liquid crystal detergent compositions helps to make such compositions resist freezing at low temperatures.

In accordance with the present invention a liquid detergent composition containing an abrasive, suitable at room temperature or colder, for pre-treating and cleaning materials soiled with lipophilic soil, is in liquid crystal form and comprises synthetic organic surface active agents, a cosurfactant, a solvent for the soil, and water.

5 The invention also relates to processes for treating items and materials soiled with lipophilic soil with compositions of this invention to loosen or remove such soil, by applying to the locus of such soil on such material a soil loosening or removing amount of an invented composition. In another aspect of the invention lipophilic soil is absorbed from the soiled surface into the liquid crystal.

10 In recent years all-purpose liquid detergents have become widely accepted for cleaning hard surfaces, e.g., painted woodwork and panels, tiled walls, wash bowls, bathtubs, linoleum or tile floors, washable wall paper, etc.. Such all-purpose liquids comprise clear and opaque aqueous mixtures of water-soluble synthetic organic detergents and water-soluble detergent builder salts. In order to achieve comparable
15 cleaning efficiency with granular or powdered all-purpose cleaning compositions, use of water-soluble inorganic phosphate builder salts was favored in the prior art all-purpose liquids. For example, such early phosphate-containing compositions are described in U.S. Patent Nos. 2,560,839; 3,234,138; 3,350,319; and British Patent No. 1,223,739.

In view of the environmentalist's efforts to reduce phosphate levels in ground
20 water, improved all-purpose liquids containing reduced concentrations of inorganic phosphate builder salts or non-phosphate builder salts have appeared. A particularly useful self-opacified liquid of the latter type is described in U.S. Patent No. 4,244,840.

However, these prior art all-purpose liquid detergents containing detergent
builder salts or other equivalent tend to leave films, spots or streaks on cleaned
25 unrinsed surfaces, particularly shiny surfaces. Thus, such liquids require thorough rinsing of the cleaned surfaces which is a time-consuming chore for the user.

In order to overcome the foregoing disadvantage of the prior art all-purpose liquid, U.S. Patent No. 4,017,409 teaches that a mixture of paraffin sulfonate and a reduced concentration of inorganic phosphate builder salt should be employed.

However, such compositions are not completely acceptable from an environmental point of view based upon the phosphate content. On the other hand, another alternative to achieving phosphate-free all-purpose liquids has been to use a major proportion of a mixture of anionic and nonionic detergents with minor amounts of glycol ether solvent and organic amine as shown in U.S. Patent NO. 3,935,130. Again, this approach has not been completely satisfactory and the high levels of organic detergents necessary to achieve cleaning cause foaming which, in turn, leads to the need for thorough rinsing which has been found to be undesirable to today's consumers.

Another approach to formulating hard surfaced or all-purpose liquid detergent composition where product homogeneity and clarity are important considerations involves the formation of oil-in-water (o/w) microemulsions which contain one or more surface-active detergent compounds, a water-immiscible solvent (typically a hydrocarbon solvent), water and a "cosurfactant" compound which provides product stability. By definition, an o/w microemulsion is a spontaneously forming colloidal dispersion of "oil" phase particles having a particle size in the range of 25 to 800 Å in a continuous aqueous phase.

In view of the extremely fine particle size of the dispersed oil phase particles, microemulsions are transparent to light and are clear and usually highly stable against phase separation.

Patent disclosures relating to use of grease-removal solvents in o/w microemulsions include, for example, European Patent Applications EP 0137615 and EP 0137616 - Herbots et al; European Patent Application EP 0160762 - Johnston et al; and U.S. Patent No. 4,561,991 - Herbots et al. Each of these patent disclosures also teaches using at least 5% by weight of grease-removal solvent.

It also is known from British Patent Application GB 2144763A to Herbots et al, published March 13, 1985, that magnesium salts enhance grease-removal performance of organic grease-removal solvents, such as the terpenes, in o/w microemulsion liquid detergent compositions. The compositions of this invention described by Herbots et al.

require at least 5% of the mixture of grease-removal solvent and magnesium salt and preferably at least 5% of solvent (which may be a mixture of water-immiscible non-polar solvent with a sparingly soluble slightly polar solvent) and at least 0.1% magnesium salt.

- 5 The following representative prior art patents also relate to liquid detergent cleaning compositions in the form of o/w microemulsions: U.S. Patents Nos. 4,472,291 - Rosario; 4,540,448 - Gautier et al; 3,723,330 - Sheflin; et al.

 Liquid detergent compositions which include terpenes, such as d-limonene, or other grease-removal solvent, although not disclosed to be in the form of o/w
10 microemulsions, are the subject matter of the following representative patent documents: European Patent Application 0080749; British Patent Specification 1,603,047; and U.S. Patent Nos. 4,414,128 and 4,540,505. For example, U.S. Patent No. 4,414,128 broadly discloses an aqueous liquid detergent composition characterized by, by weight:

- 15 (a) from 1% to 20% of a synthetic anionic, nonionic, amphoteric or zwitterionic surfactant or mixture thereof;
- (b) from 0.5% to 10% of a mono- or sesquiterpene or mixture thereof, at a weight ratio of (a):(b) being in the range of 5:1 to 1:3; and
- (c) from 0.5% to 20% of a polar solvent having a solubility in water at 15°C in
20 the range of from 0.2% to 10%. Other ingredients present in the formulations disclosed in this patent include from 0.05% to 10% by weight of an alkali metal, ammonium or alkanolammonium soap of a C₁₃-C₂₄ fatty acid; a calcium sequestrant from 0.5% to 13% by weight; non-aqueous solvent, e.g., alcohols and glycol ethers, up to 10% by weight; and hydrotropes, e.g., urea, ethanolamines, salts of lower alkylaryl sulfonates,
25 up to 10% by weight. All of the formulations shown in the Examples of this patent include relatively large amounts of detergent builder salts which are detrimental to surface shine.

U.S. Patent 5,035,826 teaches liquid crystal compositions containing nonionic surfactants but these compositions exhibit thermal stability in the limited temperature range of 19°C to 36°C.

Summary of the Invention

5 The present invention relates to improved, liquid crystal detergent compositions containing an abrasive. The compositions have improved scouring ability and interfacial tension which improves the cleaning of hard surface such as plastic, vitreous and metal surfaces having a shiny finish, oil stained floors, automotive engines and other engines. More particularly, the improved cleaning compositions exhibit good scouring power and
10 grease soil removal properties due to the improved interfacial tensions and leave the cleaned surfaces shiny without the need of or requiring only minimal additional rinsing or wiping. The latter characteristic is evidenced by little or no visible residues on the unrinsed cleaned surfaces and, accordingly, overcomes one of the disadvantages of prior art products.

15 Surprisingly, these desirable results are accomplished even in the absence of polyphosphate or other inorganic or organic detergent builder salts and also in the complete absence or substantially complete absence of grease-removal solvent.

In one aspect, the invention generally provides a stable, liquid crystal, hard surface cleaning composition especially effective in the removal of oily and greasy oil.

20 The liquid crystal composition includes, on a weight basis:

2% to 20% of an ethoxylated alkyl ether sulfate surfactant;

2% to 15% of a water-mixable cosurfactant having either limited ability or substantially no ability to dissolve oily or greasy soil;

15% to 30% of a sodium salt of a C₁₀-C₂₀ paraffin sulfonate;

25 0 to 6% of a magnesium salt such as magnesium sulfate heptahydrate or magnesium chloride;

4% to 10% of a perfume, essential oil, or water insoluble hydrocarbon having 6 to 18 carbon atoms;

0 to 20% of an abrasive; and

the balance being water, wherein the liquid crystal detergent composition does not contain any nonionic surfactant, and the liquid detergent composition has a storage modulus equal to or higher than one Pascal (1 Newton/sq. m.), more preferably higher than 10 Pascal at a temperature of 20°C to 40°C at a strain of 0.1% to 5% at a frequency of 10 radians per second as measured on a Carri-Med CS Rheometer and is thermally stable and exist as a clear liquid crystal in the temperature range from 8°C to 43°C, more preferably 4°C to 43°C.

Detailed Description of the Invention

The present invention relates to a stable liquid crystal detergent composition comprising approximately by weight: 2% to 20% of an ethoxylated alkyl ether sulfate, 2% to 15% of a cosurfactant, 15% to 30% of a sodium salt of a C₁₀-C₂₀ paraffin sulfonate, 4% to 10% of a water insoluble hydrocarbon, essential oil or a perfume, 0 to 20% of an abrasive, 0 to 6% of a magnesium salt such as magnesium sulfate heptahydrate or magnesium chloride, and the balance being water, wherein the liquid detergent composition does not contain any nonionic surfactant and the liquid detergent composition has a storage modulus equal to or higher than one Pascal (1 Newton/sq. m.), more preferably higher than 10 Pascal at a temperature of 20°C to 40°C at a strain of 0.1% to 5% at a frequency of 10 radians per second as measured on a Carri-Med CS Rheometer and is thermally stable and exist as a liquid crystal in the temperature range from 10°C to 45°C, more preferably 4°C to 43°C and a complex viscosity at 25°C of at least 2.5, more preferably 3.0 Pascal seconds.

According to the present invention, the role of the water insoluble hydrocarbon can be provided by a non-water-soluble perfume. Typically, in aqueous based compositions the presence of a solubilizers, such as alkali metal lower alkyl aryl sulfonate hydrotrope, triethanolamine, urea, etc., is required for perfume dissolution, especially at perfume levels of 1% and higher, since perfumes are generally a mixture of fragrant essential oils and aromatic compounds which are generally not water-soluble.

As used herein and in the appended claims the term "perfume" is used in its ordinary sense to refer to and include any non-water soluble fragrant substance or mixture of substances including natural (i.e., obtained by extraction of flower, herb, blossom or plant), artificial (i.e., mixture of natural oils or oil constituents) and
5 synthetically produced substance) odoriferous substances. Typically, perfumes are complex mixtures of blends of various organic compounds such as alcohols, aldehydes, ethers, aromatic compounds and varying amounts of essential oils (e.g., terpenes) such as from 0% to 80%, usually from 10% to 70% by weight, the essential oils themselves being volatile odoriferous compounds and also serving to dissolve the other
10 components of the perfume.

Quite surprisingly although the perfume is not, per se, a solvent for greasy or oily soil, --even though some perfumes may, in fact, contain as much as 80% of terpenes which are known as good grease solvents -- the inventive compositions in dilute form have the capacity to solubilize up to 10 times or more of the weight of the perfume of
15 oily and greasy soil, which is removed or loosened from the hard surface by virtue of the action of the anionic and nonionic surfactants, said soil being taken up into the oil phase of the o/w microemulsion.

In the present invention the precise composition of the perfume is of no particular consequence to cleaning performance so long as it meets the criteria of water
20 immiscibility and having a pleasing odor. Naturally, of course, especially for cleaning compositions intended for use in the home, the perfume, as well as all other ingredients, should be cosmetically acceptable, i.e., non-toxic, hypoallergenic, etc.

The hydrocarbon such as a perfume is present in the liquid crystal composition in an amount of from 4% to 10% by weight, preferably from 4% to 8% by weight. If the
25 amount of hydrocarbon (perfume) is less than 4% by weight it becomes difficult to form the liquid crystal. If the hydrocarbon (perfume) is added in amounts more than 10% by weight, the cost is increased without any additional cleaning benefit and, in fact, with some diminishing of cleaning performance insofar as the total amount of greasy or oily

soil which can be taken up in the oil phase of the micro emulsion will decrease proportionately.

Furthermore, although superior grease removal performance will be achieved for perfume compositions not containing any terpene solvents, it is apparently difficult for
5 perfumers to formulate sufficiently inexpensive perfume compositions for products of this type (i.e., very cost sensitive consumer-type products) which includes less than 20%, usually less than 30%, of such terpene solvents.

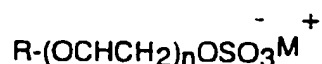
Thus, merely as a practical matter, based on economic consideration, the liquid crystal cleaning compositions of the present invention may often include as much as
10 0.2% to 7% by weight, based on the total composition, of terpene solvents introduced thereunto via the perfume component. However, even when the amount of terpene solvent in the cleaning formulation is less than 1.5% by weight, such as up to 0.6% by weight or 0.4% by weight or less, satisfactory grease removal and oil removal capacity is provided by the inventive compositions.

15 In place of the perfume in either the microemulsion composition or the all purpose hard surface cleaning composition at the same previously defined concentrations that the perfume was used in either the microemulsion or the all purpose hard surface cleaning composition one can employ an essential oil or a water insoluble organic compound such as a water insoluble hydrocarbon having 6 to 18 carbon such
20 as a paraffin or isoparaffin such as isoparH, isodecane, alpha-pinene, beta-pinene, decanol and terpineol.

Suitable essential oils are selected from the group consisting of: Anethole 20/21 natural, Aniseed oil china star, Aniseed oil globe brand, Balsam (Peru), Basil oil (India), Black pepper oil, Black pepper oleoresin 40/20, Bois de Rose (Brazil) FOB, Borneol
25 Flakes (China), Camphor oil, White, Camphor powder synthetic technical, Cananga oil (Java), Cardamom oil, Cassia oil (China), Cedarwood oil (China) BP, Cinnamon bark oil, Cinnamon leaf oil, Citronella oil, Clove bud oil, Clove leaf, Coriander (Russia), Coumarin 69°C (China), Cyclamen Aldehyde, Diphenyl oxide, Ethyl vanilin, Eucalyptol, Eucalyptus oil, Eucalyptus citriodora, Fennel oil, Geranium oil, Ginger oil, Ginger

oleoresin (India), White grapefruit oil, Guaiacwood oil, Gurjun balsam, Heliotropin, Isobornyl acetate, Isolongifolene, Juniper berry oil, L-methyl acetate, Lavender oil, Lemon oil, Lemongrass oil, Lime oil distilled, Litsea Cubeba oil, Longifolene, Menthol crystals, Methyl cedryl ketone, Methyl chavicol, Methyl salicylate, Musk ambrette, Musk
 5 ketone, Musk xylol, Nutmeg oil, Orange oil, Patchouli oil, Peppermint oil, Phenyl ethyl alcohol, Pimento berry oil, Pimento leaf oil, Rosalin, Sandalwood oil, Sandenol, Sage oil, Clary sage, Sassafras oil, Spearmint oil, Spike lavender, Tagetes, Tea tree oil, Vanilin, Vetyver oil (Java), Wintergreen

The ethoxylated alkyl ether sulfate surfactants which may be used in the
 10 composition of this invention are water soluble salts such as sodium, potassium, ammonium, triethanolamine and ethanolammonium salts of an C₈-18 ethoxylated alkyl ether sulfate surfactants have the structure:



15 wherein n is about 0 (if n = 0 SLS) to about 5 and R is an alkyl group having about 8 to about 18 carbon atoms, more preferably 12 to 15 and natural cuts, for example, C₁₂-14; C₁₂-15 and M is an ammonium cation or a metal cation, most preferably sodium. The ethoxylated alkyl ether sulfate surfactant is present in the composition at a concentration of about 2% to about 20% by weight, more preferably about 3% to 15%
 20 by weight.

The ethoxylated alkyl ether sulfate may be made by sulfating the condensation product of ethylene oxide and C₈-10 alkanol, and neutralizing the resultant product. The ethoxylated alkyl ether sulfates differ from one another in the number of carbon atoms in the alcohols and in the number of moles of ethylene oxide reacted with one
 25 mole of such alcohol. Preferred ethoxylated alkyl ether polyethenoxy sulfates contain 12 to 15 carbon atoms in the alcohols and in the alkyl groups thereof, e.g., sodium myristyl (3 EO) sulfate.

Ethoxylated C₈-18 alkylphenyl ether sulfates containing from 2 to 6 moles of ethyl ne oxid in the molecule are also suitable for use in the invention compositions.

These detergents can be prepared by reacting an alkyl phenol with 2 to 6 moles of ethylene oxide and sulfating and neutralizing the resultant ethoxylated alkylphenol. The concentration of the ethoxylated alkyl ether sulfate surfactant is about 1 to about 8 wt. %.

5 The anionic sulfonate surfactants which may be used in the detergent of this invention are water soluble such as triethanolamine and include the sodium, potassium, ammonium and ethanolammonium salts of linear C₈-C₁₆ alkyl benzene sulfonates; C₁₀-C₂₀ paraffin sulfonates and alpha olefin sulfonates containing about 10-24 carbon atoms. The preferred anionic sulfonate surfactant is a C₁-20 paraffin sulfonate present
10 in the composition at a concentration of about 15% to 30 wt. %, more preferably 17% to 25 wt. %.

 The paraffin sulfonates may be monosulfonates or di-sulfonates and usually are mixtures thereof, obtained by sulfonating paraffins of 10 to 20 carbon atoms. Preferred paraffin sulfonates are those of C₁₂-18 carbon atoms chains, and more preferably they
15 are of C₁₄-17 chains. Paraffin sulfonates that have the sulfonate group(s) distributed along the paraffin chain are described in U.S. Patents 2,503,280; 2,507,088; 3,260,744; and 3,372,188; and also in German Patent 735,096. Such compounds may be made to specifications and desirably the content of paraffin sulfonates outside the C₁₄-17 range will be minor and will be minimized, as will be any contents of di- or poly-sulfonates.

20 Examples of suitable other sulfonated anionic detergents are the well known higher alkyl mononuclear aromatic sulfonates, such as the higher alkylbenzene sulfonates containing 9 to 18 or preferably 9 to 16 carbon atoms in the higher alkyl group in a straight or branched chain, or C₈-15 alkyl toluene sulfonates. A preferred alkylbenzene sulfonate is a linear alkylbenzene sulfonate having a higher content of 3-
25 phenyl (or higher) isomers and a correspondingly lower content (well below 50%) of 2-phenyl (or lower) isomers, such as those sulfonates wherein the benzene ring is attached mostly at the 3 or higher (for example 4, 5, 6 or 7) position of the alkyl group and the content of the isomers in which the benzene ring is attached in the 2 or 1

position is correspondingly low. Preferred materials are set forth in U.S. Patent 3,320,174, especially those in which the alkyls are of 10 to 13 carbon atoms.

The major class of compounds found to provide highly suitable cosurfactants for the liquid crystals over temperature ranges extending from 5°C to 43°C for instance are glycerol, ethylene glycol, water-soluble polyethylene glycols having a molecular weight of 300 to 1000, polypropylene glycol of the formula $\text{HO}(\text{CH}_2\text{CHCH}_2\text{O})_n\text{H}$ wherein n is a number from 2 to 18, mixtures of polyethylene glycol and polypropyl glycol (Synalox) and mono C₁-C₆ alkyl ethers and esters of ethylene glycol and propylene glycol having the structural formulas $\text{R}(\text{X})_n\text{OH}$ and $\text{R}_1(\text{X})_n\text{OH}$ wherein R is C₁-C₆ alkyl group, R_1 is C₂-C₄ acyl group, X is $(\text{OCH}_2\text{CH}_2)$ or $(\text{OCH}_2(\text{CH}_3)\text{CH})$ and n is a number from 1 to 4, diethylene glycol, triethylene glycol, an alkyl lactate, wherein the alkyl group has 1 to 6 carbon atoms, 1 methoxy-2-propanol, 1 methoxy-3-propanol, and 1 methoxy 2-, 3- or 4-butanol.

Representative members of the polypropylene glycol include dipropylene glycol and polypropylene glycol having a molecular weight of 200 to 1000, e.g., polypropylene glycol 400. Other satisfactory glycol ethers are ethylene glycol monobutyl ether (butyl cellosolve), diethylene glycol monobutyl ether (butyl carbitol), triethylene glycol monobutyl ether, mono, di, tri propylene glycol monobutyl ether, tetraethylene glycol monobutyl ether, mono, di, tripropylene glycol monomethyl ether, propylene glycol monomethyl ether, ethylene glycol monohexyl ether, diethylene glycol monohexyl ether, propylene glycol tertiary butyl ether, ethylene glycol monoethyl ether, ethylene glycol monomethyl ether, ethylene glycol monopropyl ether, ethylene glycol monopentyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol monopropyl ether, diethylene glycol monopentyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, triethylene glycol monopropyl ether, triethylene glycol monopentyl ether, triethylene glycol monohexyl ether, mono, di, tripropylene glycol monoethyl ether, mono, di tripropylene glycol monopropyl ether, mono, di, tripropylene glycol monopentyl ether, mono, di, tripropylene glycol monohexyl ether, mono, di, tributylene glycol mono methyl ether, mono, di, tributylene glycol

monoethyl ether, mono, di, tributylene glycol monopropyl ether, mono, di, tributylene glycol monobutyl ether, mono, di, tributylene glycol monopentyl ether and mono, di, tributylene glycol monohexyl ether, ethylene glycol monoacetate and dipropylene glycol propionate. Tripropylene glycol n-butyl ether is the preferred cosurfactant because of its hydrophobic character.

The amount of cosurfactant required to stabilize the liquid crystal compositions will, of course, depend on such factors as the surface tension characteristics of the cosurfactant, the type and amounts of the primary surfactants and perfumes, and the type and amounts of any other additional ingredients which may be present in the composition and which have an influence on the thermodynamic factors enumerated above. Generally, amounts of cosurfactant used in the liquid crystal composition is in the range of from 1% to 30%, preferably from 2% to 20%, especially preferably from 3% to 16%, by weight provide stable dilute liquid crystal composition for the above-described levels of primary surfactants and perfume and any other additional ingredients as described below.

The instant liquid crystal compositions contain about 0 to 20 wt. %, more preferably 1 to 10 wt. % of an abrasive selected from the group consisting of amorphous hydrated silica calcite and polyethylene powder particles and mixtures thereof.

The used amorphous silica (oral grade) to enhance the scouring ability of the liquid crystal gel was provided by Zeoffin. The mean particles size of Zeoffin silica is 8 up to 10 mm. Its apparent density is 0.32 up to 0.37 g/ml.

Another silica is Tixosil 103 made by Rhone-Poulenc. An amorphous hydrated silica from Crosfield of different particles sizes (9, 15 and 300 mm), and same apparent density was also used.

An amorphous hydrated silica from Crosfield of different particles sizes (9, 15 and 300 mm), and same apparent density was also used.

The polyethylene powder used in the instant invention has a particle size of about 200 to about 500 microns and a density of about 0.91 to about 0.99 g/liter, more preferably about 0.94 to about 0.96.

Another preferred abrasive is calcite used at a concentration of about 0 to 20 wt. %, more preferably 1 wt. % to 10 wt. % is manufactured by J. M. Huber Corporation of Illinois. Calcite is a limestone consisting primarily of calcium carbonate and 1% to 5% of magnesium carbonate which has a mean particle size of 5 microns and oil absorption (rubout) of about 10 and a hardness of about 3.0 Mohs.

In addition to their excellent scouring ability and capacity for cleaning greasy and oily soils, the low pH liquid crystal formulations along with abrasives also exhibit excellent cleaning performance and removal of soap scum and lime scale in neat (undiluted) as well as in diluted usage.

The instant composition contains about 0 to about 6 wt. %, more preferably about 1 to about 5 wt. % of a magnesium salt such as magnesium chloride and/or magnesium sulfate heptahydrate and mixtures thereof.

The final essential ingredient in the inventive liquid crystal compositions having improved interfacial tension properties is water. The proportion of water in the liquid crystal detergent composition generally is in the range of 20% to 97%, preferably 70% to 97% by weight.

Enzymes are used for many purposes in various fields where biochemical reactions occur and are optionally useful in the instant compositions. In general, an enzyme can be described as a catalyst capable of permitting a biochemical reaction to quickly occur and can be classified according to the type of reaction they catalyze. Enzymes are characterized by a high specificity, that is to say, each enzyme can catalyze a single reaction of one substance or a very small number of closely related substances.

Examples of enzymes suitable for optionally being used in the cleaning compositions of this invention include lipases, proteases, peptidases, amylases (amylolytic enzymes) and others which degrade, alter or facilitate the degradation or

alteration of biochemical soils and stains encountered in cleansing situation so as to remove more easily the soil or stain from the object being washed to make the soil or stain more removable in a subsequent cleansing step. Both degradation and alteration can improve soil removability. Well known and preferred examples of these enzymes are proteases, lipases and amylases. Examples of such enzymes include Termamyl® amylase; Esperase® protease and Savinase® protease all supplied by Novo Industri A/S Copenhagen, Denmark. The enzyme may be used in the instant composition at a concentration from 0 to 5%, preferably 0.1% to 3 wt. %.

If an enzyme is used in the instant composition an enzyme stabilization system of 0.1 to 4 wt. % of borax and 0.05 to 0.5 wt. % of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ can be employed.

The instant compositions having a minimum foam height at 55 rotations at 40°C of at least 150 ml, more preferably at least 160 ml. The test solution is 0.75 grams of LDL liter of water and 10 g/l of corn oil per liter of water having a hardness of 300 PPM.

A composition of this invention is in a liquid crystal state when it is of lyotropic structure, is transparent or slightly turbid (opalescent) but not opaque, and has a storage modulus equal to or higher than one Pascal (1 Newton/sq. m.), more preferably higher than 10 Pascal and most preferably higher than 20 Pascal and when measured at a temperature of 20 to 40°C, at a frequency of ten radians per second and at a strain of 0.1 to 5%. The rheological behavior of the compositions of this invention were measured at 25°C by means of a Carri-Med CS Rheometer. In making the measurement, a cone and plate are used at a cone angle of 2 degrees: 0 minutes: 0 seconds with a cone diameter of 6.0 cm, measurement system gap of 52.0 micro m and a measurement system inertia of 17.02 micro Nm sec⁻².

To make the liquid crystal compositions of the invention is relatively simple because they tend to form spontaneously with little need for the addition of energy to promote transformation to the liquid crystal state. However, to promote uniformity of the composition mixing will normally be undertaken and it has been found desirable first to mix the surfactants and cosurfactant with the water, followed by admixing of the lipophilic component, usually a hydrocarbon (but esters or mixtures of hydrocarbons

and esters may also be employed). It is not necessary to employ heat and most mixings are preferably carried out at about room temperature (20-25°C).

The invented compositions may be applied to such surfaces by pouring onto them, by application with a cloth or sponge, or by various other contacting means but it is preferred to apply them in the form of a spray by spraying them onto the substrate from a hand or finger pressure operated sprayer or squeeze bottle. Such application may be onto hard surfaces, such as dishes, walls or floors, from which lipophilic (usually greasy or oily) soil is to be removed, or may be onto fabrics, such as laundry, which has previously been stained with lipophilic soils, such as motor oil. The invented compositions may be used as detergents and as such may be employed in the same manner in which liquid detergents are normally utilized in dishwashing, floor and wall cleaning and laundering, but it is preferred that they be employed as pre-spotting agents too, in which applications they are found to be extremely useful in loosening the adhesions of lipophilic soils to substrates, thereby promoting much easier cleaning with application of more of the same invented detergent compositions or by applications of different commercial detergent compositions, in liquid, bar or particulate forms.

The various advantages of the invention have already been set forth in some detail and will not be repeated here. However, it will be reiterated that the invention relates to the important discovery that effective liquid detergent compositions can be made in the liquid crystal state and that because they are in such state they are especially effective in removing lipophilic soils from substrates and also are effective in removing from substrates non-lipophilic materials. Such desirable properties of the liquid crystal detergent compositions of this invention make them ideal for use as pre-spotting agents and detergents for them ideal for use as pre-spotting agents and detergents for removing hard-to-remove soils from substrates in various hard and soft surface cleaning operations.

The following examples illustrate but do not limit the invention. Unless otherwise indicated, all parts in these examples, in the specification and in the appended claims are by weight and all temperature are in °C.

Example I

The following formulas (wt. %) were made at 25°C by simple mixing.

	A	B	C	Premium Competitive Product
Sodium C ₁₃ -C ₁₇ paraffin sulfonate	20	22.5	20	
C ₁₂₋₁₄ ethoxylated alkyl ether sulfate (2 EO)	5	7.5	5	
D-Limonene	7	7	7	
MgSO ₄ ·7H ₂ O		4.2		
Tripropylene glycol n-butyl ether	11	3	7	
Borax			3	
CaCl ₂ ·2H ₂ O			0.4	
Enzyme			0.8	
Calcite		5		
Miniplat	32	47	32	40
Gardner neat	Better	Better	Better	Std.
Heavy greasy soil	Better	Better	Better	Std.

- The invention has been described with respect to various embodiments and illustrations of it but is not to be considered as limited to these because it is evident that one of skill in the art with the present specification before him or her will be able to utilize substitutes and equivalents without departing from the invention.

1. Miniplat test

- Miniplat test aims at assessing foam stability / duration of a dish liquid solution (1.25 g/l) in presence of a fat (Crisco Vegetal shortening ex P&G). The higher the number the better the product.

2. Gardner neat on baked on soils

- This test aims at assessing the cleaning power of a dish product on a mixed baked on soil. Soil is made of egg yolk, margarin, beef extract and instant flour spread with a brush on a tile and put in an oven at 270 °C for 10 minutes. the test uses a gardner washability machine and measures the number of strokes needed to clean the surface of a tile made of formica. In each experiment a reference (premium competitive product) is included and results are given in comparison to this reference.

3. Heavy greasy soil.

- This test aims at assessing the auto active power (capacity to quickly absorb oil under static conditions) of a dish liquid on a heavy greasy soil (hydrogenated beef

tallow). the results are always given in comparison to a reference (premium competitive product)

What is Claimed is:

1. A liquid crystal detergent composition which comprises by weight:
 - (a) about 15% to about 30% of a sodium paraffin sulfonate;
 - (b) about 2% to about 20% of a water soluble salt of an ethoxylated C₈-18
- 5 alkyl ether sulfate surfactant;
 - (c) about 0 to about 20% of an abrasive;
 - (d) about 2 % to about 15% of a cosurfactant;
 - (e) about 4% to about 10% of a water insoluble organic compound selected
- 10 from the group consisting of perfumes, essential oils and water insoluble hydrocarbons having about 8 to about 18 carbon atoms; and
 - (f) the balance being water, said liquid crystal detergent composition has a storage modulus measured at a temperature between 20°C to 40°C, at a strain of 0.1% to 5% and a frequency of 10 radians/second of at least about one Pascal.
2. The composition of Claim 1 wherein said water soluble salt of said
- 15 ethoxylated C₈-18 alkyl ether sulfate surfactant has a cation selected from the group consisting of sodium, potassium and ammonium.
3. The composition of Claim 2, wherein said water insoluble hydrocarbon is d-limonene, selected from the group consisting of d-limonene, alpha-terpineol, alpha-pinene, and beta pinene and mixtures thereof.
- 20 4. The composition of Claim 3, wherein said cosurfactant is tripropylene glycol n-butyl ether.
5. The composition of Claim 1, wherein said abrasive is selected from the group consisting of calcite, amorphous hydrated silica or polyethylene powder and mixtures thereof.
- 25 6. A process for treating materials soiled with lipophilic soil to loosen or remove it which comprises applying to the locus of such soil on such material a soil loosening or removing amount of a composition according to Claim 1.
7. A process according to Claim 5 wherein the composition is applied as a pre-treatment to material soiled with hard-to-remove lipophilic soil at the locus thereof

on the material, after which application the soil is removed by application of the same or a different detergent composition and water.

INTERNATIONAL SEARCH REPORT

Invent. Application No
PCT/US 97/09851

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C11D17/00 C11D1/37 C11D3/14 C11D3/16 C11D3/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB 2 280 450 A (PROCTER & GAMBLE) 1 February 1995 see page 3, line 10 - page 9, line 28 ---	1-7
A	EP 0 125 711 A (UNILEVER NV ;UNILEVER PLC (GB)) 21 November 1984 see example 4 ---	1-7
A	EP 0 637 629 A (COLGATE PALMOLIVE CO) 8 February 1995 see page 5, line 27 - page 6, line 24 ---	1-7
A	EP 0 530 708 A (ALBRIGHT & WILSON) 10 March 1993 see page 9, line 30 - line 55 ---	1-7
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Interr. Int'l Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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